Synthesis and Structural Characterization of a New Two-dimensional Organic-Inorganic Hybrid Molybdoarsenate: [Cu(en)$_2$][(CuO$_6$)Mo$_6$O$_{18}$(As$_3$O$_3$)$_2$]

Qiang Wu$, Qixia Han$^b$, Lijun Chen$^c$, Pengtao Ma$^b$, and Jingyang Niu$^b$

$^a$ Medical School, Henan University, Kaifeng 475001, P. R. China
$^b$ Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P. R. China
$^c$ Basic Experimental Teaching Center, Henan University, Kaifeng 475004, P. R. China

Reprint requests to Prof. Jingyang Niu. Fax: +86-378-2853650. E-mail: jyniu@henu.edu.cn

Z. Naturforsch. 2010, 65b, 163 – 167; received November 28, 2009

A new organic-inorganic hybrid molybdoarsenate constructed from a unit with two (As$_3$O$_3$) rings capping Anderson-type moieties, [Cu(en)$_2$][(CuO$_6$)Mo$_6$O$_{18}$(As$_3$O$_3$)$_2$] (en = ethylenediamine), has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction and thermogravimetric analysis. The compound crystallizes monoclinically, space group $P2_1/c$, with unit cell dimensions $a = 9.1541(7)$, $b = 19.6348(14)$, $c = 14.5205(8)$ Å, $\beta = 129.082(3)^\circ$, $V = 364.20(4)$ Å$^3$, $Z = 2$, $T = 296(2)$ K. Complex 1 represents the first example of a 2D network of a POM polymer where [(CuO$_6$)Mo$_6$O$_{18}$(As$_3$O$_3$)$_2$]$^{2-}$ building blocks are connected by complex fragments {Cu(en)$_2$}$^{2+}$.

Key words: Polyoxometalate, Hydrothermal Synthesis, Crystal Structure, Anderson-type Unit

Introduction

Polyoxometalates (POMs) are a large family of metal-oxygen clusters with surprising compositional variability, electronic versatility and topological diversity [1]. These features endow them with applications in catalysis, medicine, material science, and photochemistry [2, 3]. One of the challenges in the synthesis of POM chemistry is to find multifunctional polyoxoanion building blocks and to connect them to one-, two-, or even three-dimensional extended solid frameworks.

It is well-known that Anderson-type polyoxoanions have abundant terminal oxygen atoms and can be used as multifunctional building blocks. Since the first Anderson-type anion [TeMo$_6$O$_{24}$$^{6-}$] was reported in 1937 [4], these polyoxoanions have been extensively explored to construct 1D, 2D and even 3D compounds [5 – 12]. For example, in 2002, Das and coworkers reported the first 1D POM [La(H$_2$O)$_7$Al(OH)$_6$Mo$_6$O$_{18}$]·4H$_2$O [5], and a 1D spiral-shaped inorganic-organic hybrid chain-like structure [Cu(2,2′-bipy)(H$_2$O)$_2$Al(OH)$_6$Mo$_6$O$_{18}$]·5H$_2$O. In 2004, Krebs and coworkers published a series of 1D lanthanide derivatives K$_6$(TeMo$_6$O$_{24}$)·16H$_2$O ($Ln = Eu^{III}$, Gd$^{III}$) and K$_3$[Ln(H$_2$O)$_5$(TeMo$_6$O$_{24}$)]·6H$_2$O ($Ln = Tb^{III}$, Dy$^{III}$, Ho$^{III}$, Er$^{III}$) [8]. Later, Wang and coworkers published a series of 2D and 3D extended POM frameworks [(H$_2$O)$_5$Na$_2$(C$_6$NO$_2$H$_4$)(C$_6$NO$_2$H$_5$)$_3$-Ag$_2$][Ag$_2$Mo$_6$O$_{24}$(H$_2$O)$_4$] $\cdot$ 6.25H$_2$O [10] and [(H$_2$O)$_4$Ag$_2$][(OH)$_5$Mo$_6$O$_{18}$]·3H$_2$O [11], and networks [(H$_2$O)$_4$Na$_2$(C$_6$NO$_2$H$_5$)$_3$-Ag$_2$][IMo$_6$O$_{24}$·6H$_2$O [10] and [(C$_6$H$_5$NO$_2$)$_2$Ln(H$_2$O)$_4$][IMo$_6$O$_{24}$·NO$_3$·4H$_2$O ($Ln = Ce^{III}$, La$^{III}$) [11]. Then, in 2007, Liu and coworkers reported two compounds with 1D chains constructed by alternating Anderson-type polyoxoanions and oxalate-bridged binuclear copper complexes, [Cu$_2$(bpy)$_2$(μ-ox)][M(OH)$_7$Mo$_6$O$_{18}$]$^-$ ($M = Al^{III}$, Cr$^{III}$) [12]. These compounds constitute an important subclass of inorganic chemistry with significance in the disciplines of magnetism and catalysis. However, compared to the abundance of these compounds based on typical Anderson-type POMs, examples based on two cyclic As$_3$O$_3$ groups capping Anderson-type POMs have rarely been reported. Typical examples with discrete cluster structures include [Co(H$_2$O)$_6$]$_2$[As$_5$CoMo$_6$O$_{30}$] [13], [Ni(en)$_3$$_2$$(MoIVO$_6$)Mo$_6$O$_{7}$O$_{18}$(As$_{3}$III$O_3$)$_2$·H$_2$O [14], Co$^{III}$[en$_3$]H$_2$O$_2$(Co$^{II}$O$_6$)Mo$^{VI}$O$_{18}$(As$_{3}$III$O_3$)$_2$·H$_2$O [15].
Recently, Wang and coworkers reported \((4,4′\text{-bipy})\)\(_2(Zn(4,4′\text{-bipy})\)\(_2(H_2O)\)_2\([\{ZnO_6\}(As^{III}_3O_3)_2\]Mo\(_6\)O\(_{18}\]·7H\(_2\)O\) and \([Zn(H_4.4′\text{-bipy})_2H_2O]\)[(ZnO\(_6\)\)-(As\(^{III}_3\)O\(_3\))\(_2\])Mo\(_6\)O\(_{18}\]·8H\(_2\)O \[17\], and Zhou and coworkers reported \([Cu(\text{imi})\]\(_2\)]\(_2\)[(CuO\(_6\))(As\(^{III}_3\)O\(_3\))\(_2\)]\(_2\)Mo\(_6\)O\(_{18}\]·Cu(\text{imi})\(_2\)]\(_2\) \[18\]. However, all these 3D supramolecular frameworks are constructed via hydrogen bonding interactions. Therefore, in order to extend solid framework materials constructed by units \([\{Mo\(_6\)O\(_8\]O\(_{18}\)(As\(^{III}_3\)O\(_3\))\(_2\]\(_2\]− (M = transition metal), we synthesized a new organic-inorganic hybrid molybdooarsenate \([Cu(\text{en})\]\(_2\)]\(_2\)[(CuO\(_6\)]Mo\(_6\)O\(_{18}\)(As\(^{III}_3\)O\(_3\))\(_2\])\(_2\]\(_2\]·(en = ethylenediamine) under mild hydrothermal conditions. It is the most remarkable feature of \(\textbf{1}\), that each \([\{CuO\(_6\)]Mo\(_6\)O\(_{18}\)(As\(^{III}_3\)O\(_3\))\(_2\]\(_2\]− unit acts as a 4-connected node linking four \(\{Cu(\text{en})\]\(_2\]\) groups in a centrosymmetric manner generating a two-dimensional network with \((4,4)\) topology. To the best of our knowledge, it is the first example of a 2D POM network where \([\{CuO\(_6\)]Mo\(_6\)O\(_{18}\)(As\(^{III}_3\)O\(_3\))\(_2\]\(_2\]− building blocks are connected by coordination to complex fragments \(\{Cu(\text{en})\]\(_2\]\)\(^2\).
radiation ($\lambda = 0.71073 \text{ Å}$). The structure was solved by Direct Methods using the SHELX-97 program package [19]. The remaining atoms were found from successive Fourier syntheses. Hydrogen atoms attached to carbon and nitrogen atoms were geometrically placed. Refinement was done with full-matrix least-squares on $F^2$ [19].

CCDC 743507 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif.

**Results and Discussion**

**X-Ray crystal structure**

Single-crystal X-ray diffraction analysis has revealed that the structural unit of I consists of an Anderson-type $[\text{CuO}_6\text{Mo}_6\text{O}_{18}(\text{As}_3\text{O}_3)_2]^{4-}$ unit capped by two $\text{As}_3\text{O}_3$ rings and two hexa-coordinate $[\text{Cu(en)}_2]^2^+\text{cations (Figs. 1a and 2a). Selected bond lengths and angles are collected in Table 2. Bond Valence Sum (BVS) calculations of I show that the oxidation states of all Mo, Cu and As atoms are $+6$, $+2$ and $+3$, respectively [20]. As shown in Fig. 1b, the $[\text{CuO}_6\text{Mo}_6\text{O}_{18}(\text{As}_3\text{O}_3)_2]^{4-}$ unit displays $D_{3d}$ point symmetry and is derived from the well-known Anderson anion $[\text{CuO}_6\text{Mo}_6\text{O}_{18}]^{10-}$, in which a central $\{\text{CuO}_6\}$ octahedron is hexagonally surrounded shar-
Table 3. Hydrogen bond lengths (Å) and bond angles (deg)\(^a\).

<table>
<thead>
<tr>
<th>D–H \cdots A</th>
<th>d(H \cdots A)</th>
<th>d(D \cdots A)</th>
<th>(\angle) (DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)–H(1D) \cdots O(6)(^{44})</td>
<td>2.29</td>
<td>3.189(7)</td>
<td>172.6</td>
</tr>
<tr>
<td>N(1)–H(1D) \cdots O(8)(^{44})</td>
<td>2.57</td>
<td>3.009(6)</td>
<td>110.8</td>
</tr>
<tr>
<td>N(2)–H(2C) \cdots O(3)(^{52})</td>
<td>2.16</td>
<td>2.970(6)</td>
<td>149.3</td>
</tr>
<tr>
<td>N(2)–H(2C) \cdots O(15)(^{52})</td>
<td>2.61</td>
<td>3.287(6)</td>
<td>132.2</td>
</tr>
<tr>
<td>N(2)–H(2D) \cdots O(8)(^{51})</td>
<td>2.15</td>
<td>3.018(6)</td>
<td>161.7</td>
</tr>
<tr>
<td>N(3)–H(3C) \cdots O(8)(^{51})</td>
<td>2.46</td>
<td>3.181(7)</td>
<td>137.0</td>
</tr>
<tr>
<td>N(3)–H(3D) \cdots O(1)(^{53})</td>
<td>2.48</td>
<td>3.095(6)</td>
<td>125.8</td>
</tr>
<tr>
<td>N(4)–H(4C) \cdots O(4)(^{44})</td>
<td>2.18</td>
<td>3.055(7)</td>
<td>162.2</td>
</tr>
<tr>
<td>N(4)–H(4D) \cdots O(13)(^{46})</td>
<td>2.58</td>
<td>3.302(7)</td>
<td>137.3</td>
</tr>
</tbody>
</table>

\(^a\) Symmetry transformations: \(^{41}\) \(-x,-y-1,-z+1;^{42} x+1,-y-1/2,z+1/2;^{43} x-1,-y-1/2,z-1/2;^{44} x,y+1/2,-z+1/2;^{45} x,-y-1/2,z+1/2;^{46} x,-y-1/2,z-1/2.\)

Fig. 3. TGA curve of compound I in flowing air atmosphere at 10°C min\(^{-1}\).

the oxidation state +1 of the outer Cu atoms prevents further bonding to another \([\text{CuO}_6\text{As}_3\text{O}_3\text{Mo}_6\text{O}_{18}]^{4-}\) unit, the oxidation state +2 of the Cu(2) atoms in I allows for further bonding to \([\text{CuO}_6\text{As}_3\text{O}_3\text{Mo}_6\text{O}_{18}]^{+}\) units to construct a 2D extended framework. The resulting gridlike coordination framework has (4,4) topology (Fig. 2c). Each layer shows square cavities with dimensions 8.6 \times 16.8 Å\(^2\) based on \(d_{\text{Cu-Cu}}\). Therefore, the successful synthesis of I gives guidance for the development of new coordination networks and topologies in POM chemistry. In addition, taking into account the strong hydrogen bonding interactions, a 3D supramolecular structure is generated through the N and the O atoms of the polyanions with \(N\cdots O\) distances of 2.970(6)–3.302(7) Å for I. The hydrogen bond lengths and bond angles are listed in Table 3. These hydrogen bonds make the crystal structure of compound I more stable.

**IR spectra**

In comparison with the Keggin and Dawson types, IR spectroscopic studies of Anderson polyanions are rare, and the characteristic peaks have not been strictly assigned. In the low-wavenumber regions of the IR spectrum of I, the peaks at 932, 906 and 885 cm\(^{-1}\) are attributed to the Mo=O vibrations, those at 823, 787 and 669 cm\(^{-1}\) to the Mo–O\(_{(\mu 2)}\) stretching modes, and those at 616 cm\(^{-1}\) to Cu–O\(_3\) stretching modes. Bands at 559, 533 and 461 cm\(^{-1}\) are assigned to the Mo–O\(_{(\mu 4)}\) stretching vibration. The peaks in the range...
from 1035 to 1593 cm\(^{-1}\) are attributed to the ethylene-
diamine ligand.

**Thermo-gravimetric analysis**

The thermal decomposition of compound 1 is char-
acterized by the loss of the organic groups and of
\(\text{As}_2\text{O}_3\) from 240 to 380 °C (Fig. 3). A 12.0 % weight
loss is attributed to the loss of 4 en units (calcu-
lated 12.42 %). This is followed by a weight loss of
cu. 30.04 % for the release of 3\(\text{As}_2\text{O}_3\) (calcu-
lated 30.65 %).

**Acknowledgement**

This work was supported by the National Natural Science
Foundation of China (20771034) and the Natural Science
Foundation of Henan Province (2009A150003).

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